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STEREOSELECTIVE OXIDATIVE ADDITION OF SILANES AND  
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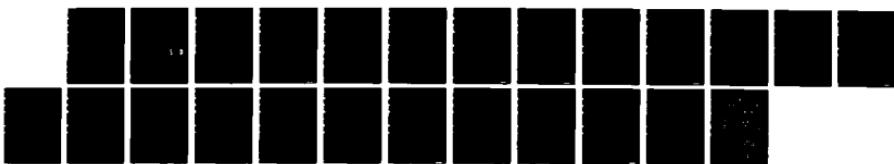
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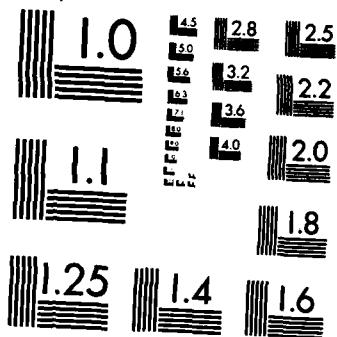
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TECHNICAL REPORT NO. 8

Stereoselective Oxidative Addition of Silanes and Hydrogen Halides

to the Iridium(I) cis-Phosphine Complexes

IrX(CO)(1,2-bis(diphenylphosphino)ethane), X = Br, CN

by

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Prepared for Publication

in the

Journal of the American Chemical Society

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## REPORT DOCUMENTATION PAGE

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## 16 ABSTRACT (Continue on reverse side if necessary and identify by block number)

The oxidative addition of silanes,  $\text{R}_n\text{Cl}_{3-n}\text{SiH}$  ( $n = 3$ ,  $\text{R} = \text{Et}$ , Ph, OEt;  $n = 2$ ,  $\text{R} = \text{Me}$ ;  $n = 1$ ,  $\text{R} = \text{Me}$ ), to the Ir(1) cis phosphine complexes  $\text{IrX}(\text{CO})_{11-2}$ ,  $\text{X} = \text{Br}$ , CN; dpp = 1,2-bis(diphenylphosphino)ethane) has been found to proceed stereoselectively under kinetic control. Of the four possible diastereomers which can form by concerted *cis* addition of the Si-H bond to the iridium(1) center, the one having hydride trans to CO and Si *trans* to P(dpp) is formed initially with 98% stereoselectivity. For  $\text{X} = \text{Br}$ , this diastereomer is not the thermodynamically favored product. Isomerization of the initially formed silyl hydride

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17 ABSTRACT (Continue on reverse side if necessary and identify by block number) product to the equilibrium mixture of diastereomers follows first order kinetics for the triphenylsilyl derivative with $k_1 = 0.015 \text{ min}^{-1}$ . The rate of isomerization for the kinetic silyl hydride adducts decreases in the order $\text{Et}_3\text{SiH} > (\text{Et}_2\text{O})_2\text{SiH} > \text{MeCl}_2\text{SiH}$ derivative not isomerizing even after prolonged heating. The most stable diastereomer for $\text{X} = \text{Br}$ has hydride trans to Br and silyl <i>trans</i> to P(dpp). For $\text{X} = \text{CN}$ , the kinetic isomer with H trans to CO and Si <i>trans</i> to P(dpp) is also the most stable isomer, although other isomers are observed to form after initial reaction. Secondary chemistry of the triethylsilyl hydride products to $\text{X} = \text{Br}$ and CN is observed over longer reaction times leading to the formation of $\text{IrX}(\text{CO})(\text{dpp})$ ( $\text{X} = \text{Br}$ ), $\text{IrH}_2(\text{SiEt}_3)$ ( $\text{X} = \text{CN}$ ), and $\text{Et}_3\text{SiSiEt}_3$ . This secondary chemistry is consistent with reductive elimination/oxidative addition sequences. The oxidative addition of $\text{HX}$ to $\text{IrX}(\text{CO})(\text{dpp})$ also proceeds stereoselectively, giving the isomer with H <i>trans</i> to $\text{X}^+$ and X <i>trans</i> to P(dpp). This diastereomer results from <i>cis</i> addition in which H-X approaches the square planar $\text{Ir}(1)$ complex with its axis parallel to $\text{X}^+-\text{Ir}-\text{P}$ . Thus, while $\text{R}_3\text{SiH}$ and $\text{HX}$ both add to $\text{IrX}(\text{CO})(\text{dpp})$ by <i>cis</i> concerted mechanism, the diastereoselection for $\text{HX}$ is opposite to that for $\text{R}_3\text{SiH}$ . It is proposed that this difference arises because the silane approach to the $\text{Ir}(1)$ complex is nucleophilic while that of $\text{HX}$ is electrophilic.	
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Interconversion of Silanes and Hydrogen Halides  
to the Iridium(I) cis-Phosphine Complexes

$\text{IrX}(\text{CO})(1,2\text{-bis}(\text{diphenylphosphino)ethane})$ , X = Br, CN

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Received

**Abstract:** The oxidative addition of silanes,  $\text{R}_n\text{Cl}_3\text{SiH}$  (n = 3, R = Et, Ph, OEt; n = 2, R = Me; n = 1, R = Me), to the Ir(I) cis-phosphine complexes  $\text{IrX}(\text{CO})(\text{dppe})$  (X = Br, CN; dppe = 1,2-bis(diphenylphosphino)ethane) has been found to proceed stereoselectively under kinetic control. Of the four possible diastereomers which can form by concerted cis addition of the Si-H bond to the Iridium(I) center, the one having hydride trans to CO and Si trans to P(dppe) is formed initially with >98% stereoselectivity. For X = Br, this diastereomer is not the thermodynamically favored product. Isomerization of the initially formed silyl hydride product to the equilibrium mixture of diastereomers follows first order kinetics for the triphenylsilyl derivative with  $k_1^{\text{H}} = 0.015/\text{min}$ . The rate of isomerization for the kinetic silyl hydride adducts decreases in the order  $\text{Et}_3\text{SiH} > \text{Ph}_3\text{SiH} > (\text{OEt})_3\text{SiH} > \text{Me}_3\text{SiH}$  with the  $\text{Me}_3\text{SiH}$  derivative not isomerizing even after prolonged heating. The most stable diastereomer for X = Br has hydride trans to Br and silyl trans to

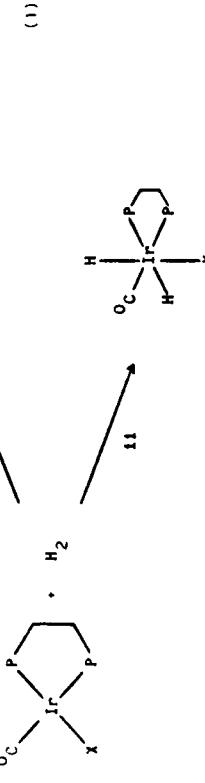
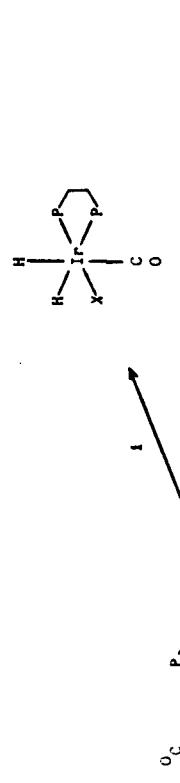
P(dppe). For X = CN, the kinetic isomer with H trans to CO and Si trans to P(dppe) is also the most stable isomer, although other isomers are observed to form after initial reaction. Secondary chemistry of the triethylsilyl hydride products for X = Br and CN is observed over longer reaction times leading to the formation of  $\text{IrH}_2(\text{CO})(\text{dppe})$  (X = Br),  $\text{IrH}_2(\text{SiEt}_3)(\text{CO})(\text{dppe})$ , and  $\text{Et}_3\text{SiSiEt}^n$ . This secondary chemistry is consistent with reductive elimination/oxidative addition sequences. The oxidative addition of HX to  $\text{IrX}(\text{CO})(\text{dppe})$  also proceeds stereoselectively, giving the isomer with H trans to X<sup>+</sup> and X trans to P(dppe). This diastereomer results from cis addition in which H-X approaches the square planar Ir(I) complex with its axis parallel to X<sup>+</sup>-Ir-P. Thus, while  $\text{R}_3\text{SiH}$  and HX both add to  $\text{IrX}(\text{CO})(\text{dppe})$  by a cis concerted mechanism, the diastereoselection for HX is opposite to that for  $\text{R}_3\text{SiH}$ . It is proposed that this difference arises because the silane approach to the Ir(I) complex is nucleophilic while that of HX is electrophilic.

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## Introduction

In previous reports we have described the kinetic stereoselectivity of  $H_2$  oxidative addition to  $IrX(CO)(dppe)$  complexes, ( $dppe = 1,2$ -bis(diphenylphosphino)ethane), which are cis-phosphine analogs of Vaska's complex, trans- $IrCl(CO)(PPh_3)_2$ .<sup>1,2</sup> This oxidative addition can proceed along two possible pathways, 1 and 11, as shown in eqn (1), leading to different diastereomers for the concerted cis addition of  $H_2$ . Pathway 1 corresponds to

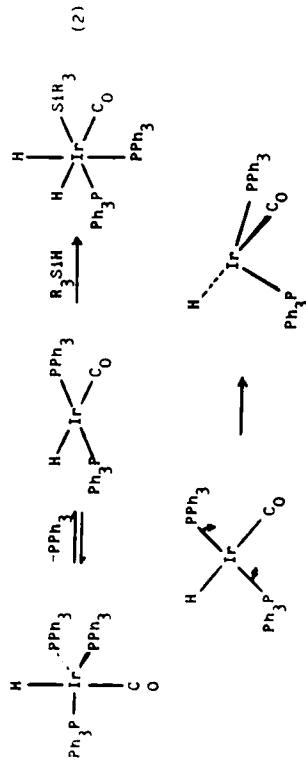


$H_2$  approach to the square planar complex with the molecular axis of  $H_2$  parallel to  $P\text{-Ir-CO}$  as shown in A. The concerted oxidative addition along 1 takes place with a bending of the trans  $P\text{-Ir-CO}$  axis so that one hydride of the product becomes trans to CO and the other trans to P. Pathway 11 corresponds to approach with the  $H_2$  molecular axis parallel to  $P\text{-Ir-X}$ , as shown in B, and addition occurs with bending of the  $P\text{-Ir-X}$  axis.



While two diastereomers for concerted  $H_2$  oxidative addition to  $IrX(CO)(dppe)$  are thus possible, we have found that for  $X = Cl, Br, I, H$ , and  $CH_3$ , the initial oxidative addition takes place diastereoselectively along pathway 1. The reaction proceeds under kinetic control as illustrated by the fact that for  $X = Cl, Br$ , and I, the diastereomer formed initially slowly equilibrates with the more stable diastereomer corresponding to oxidative addition along pathway 11. Based on the variation of X, a steric basis for the diastereoselectivity of  $H_2$  oxidative addition can be ruled out, leaving ligand electronic effects as the controlling factor in the diastereoselection process.

In order to probe more deeply the extent and basis of kinetically-controlled diastereoselectivity in oxidative additions, we have examined the reaction chemistry between  $IrX(CO)(dppe)$  and the unsymmetrical substrates  $R_3SiH$  and  $HX$ . The oxidative addition of silanes to iridium(I) complexes has been studied extensively.<sup>3-13</sup> The reaction, which represents a required step in hydrosilation catalysis, is generally viewed as a concerted cis addition.<sup>14</sup> However, this has only been demonstrated or established convincingly in a limited number of cases. In an elegant series of investigations, Harrod and coworkers have studied silane oxidative addition to  $IrH(CO)(PPh_3)_3$  kinetically and stereochemically.<sup>3,4</sup> Their analysis of the reaction in eqn (2) through the determination of activation parameters led them to the conclusion that silane oxidative addition and phosphine addition are mechanistically similar processes with activation enthalpies due mainly to deformation of the square planar complex prior to addition as shown in C.<sup>3</sup>



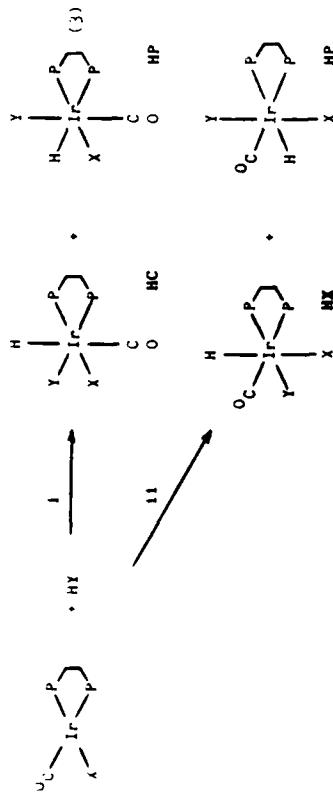
Through the use of deuterated silane substrate, Fawcett and Harrrod showed that the hydride ligand *trans* to  $\text{PPh}_3$  in the product of eqn (2) comes from the silane substrate in the *cis* addition process.<sup>4a</sup>

In a different study, Bennett, et al.,<sup>7</sup> examined silane addition to  $\text{IrCl}_3$  ( $\text{L} = \text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $\text{AsPh}_3$ ) to give the  $\text{Ir}(\text{III})$  silyl hydrides  $\text{IrHCl}(\text{SiR}_3)_n$  where  $n = 2$  or 3. In all cases, the silyl and hydride groups in the product complexes are mutually *cis*, and this result is taken as supporting, but not proving, *cis* concerted addition of silane. A definitive study of the stereochemistry of  $\text{R}_3\text{SiH}$  addition to Vaska's complex as it relates to the

mechanism of the reaction has not been performed to date because of insufficient solubility of initial  $\text{IrHCl}(\text{SiR}_3)(\text{CO})(\text{PPh}_3)_2$  products, and facile secondary reactions leading to dihydride products. However, a study by Sommer, et al., using optically active silanes  $\text{R}_3\text{Si}^{\text{D}}\text{H}$  showed that Vaska's complex promotes  $\text{Si}^{\text{D}}\text{H}/\text{Si}^{\text{D}}$  exchange with complete retention of configuration at Si, thereby giving support to the notion of *cis* concerted addition of silane to Vaska's complex.<sup>11</sup>

The mechanism of  $\text{HX}$  addition to  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  and its analogs has also been investigated.<sup>15-17</sup> Vaska observed that gaseous  $\text{HX}$  oxidatively adds to  $\text{trans-}\text{IrX}(\text{CO})(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) in the solid state to form *cis* addition products.<sup>15</sup> Blake and Kubota<sup>16</sup> found that the *cis* stereochemistry of addition also holds for the reaction in benzene or chloroform solution. In the presence of more polar solvents such as methanol, acetonitrile, water, or dimethylformamide, however, mixtures of *cis* and *trans*  $\text{HX}$  isomers are formed. Longato, et al., established a similar stereochemistry of  $\text{HX}$  addition to crystalline *trans- $\text{Ir}(\text{carb})(\text{CO})(\text{PPh}_3)_2$*  ( $\text{carb} = \text{--2-R-1,2-C}_2\text{H}_10$  or the 1,7-carborane).<sup>17</sup> The *cis* stereochemistry of addition to  $\text{Ir}(\text{carb})(\text{CO})(\text{PPh}_3)_2$  is maintained in dry non-polar solvents, but mixtures of *cis* and *trans* addition products are found in wet benzene and  $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$  solutions, and only *trans* addition is seen for the complex containing the bulky ligand  $-2\text{CH}_3-1,2-\text{B}_10\text{C}_2\text{H}_10$ . It thus appears that the stereochemistry and mechanism of  $\text{HX}$  oxidative addition to  $\text{Ir}(\text{I})$  complexes of the type  $\text{IrX}(\text{CO})_2$  depend on the reaction conditions and  $\text{Ir}(\text{I})$  ligands, with *cis* addition occurring in non-polar media and  $\text{Ir}(\text{I})$  ligands, with

For the *cis*-phosphine complexes  $\text{IrX}(\text{CO})(\text{dppe})$  used in the present study, *cis* oxidative addition of an unsymmetrical substrate  $\text{HY}$  corresponds to a double diastereoselection process in which the orientation of the  $\text{HY}$  substrate relative to the metal complex offers two possibilities for each of the pathways of addition shown in eqn (1). The four diastereomers for *cis* addition of  $\text{HY}$  to  $\text{IrX}(\text{CO})(\text{dppe})$  are shown in eqn (3). We will refer to the double diastereoselection process as diasteroisoselection (i.e., pathway 1 or 11) with specific substrate orientation. The relative orientation of  $\text{HY}$  in a *cis* concerted addition is given by the position of the hydride ligand in the product. For



oxidative addition along the P-Ir-CO axis, pathway 1, two diastereomers are possible, the first with hydride trans to CO labelled as HC and the second with hydride trans to P labelled as HP. These two diastereomers correspond respectively to HY approach to  $\text{IrX}(\text{CO})(\text{dppe})$  shown as D and E. Similarly for pathway 11 (addition along the P-Ir-X axis), diastereomers with hydride trans to



X (HX) and hydride trans to P (HP) are possible, corresponding to substrate approaches shown as F and G. This manner of labeling the diastereomers of HY



addition by pathway of addition and ligand trans to hydride will be used throughout the rest of the paper.

### Experimental Section

General. The following reagents were used as received: triethylsilane, triphenylsilane, triethoxysilane, chlorodimethylsilane, dichloromethylsilane, and tetra-n-butylammonium (TBA) bromide (Aldrich), HBr (Matheson, 99.9%), and  $^{13}\text{CO}$  (Monsanto Research Corp., 99%). Bis(triphenylphosphine)minium (PPN) cyanide,<sup>18</sup>  $\text{IrBr}(\text{CO})(\text{dppe})^2$ , and  $\text{Ir}(\text{CO})(\text{dppe})^{19}$  were prepared by established procedures. Benzene-d<sub>6</sub> and acetone-d<sub>6</sub> (Aldrich Gold Label, 99.9% D) were distilled from Na/benzophenone and Linde 4A molecular sieves, respectively, for sealed-tube NMR experiments.

Reactions were generally carried out under a nitrogen atmosphere using a Schlenk-type vacuum line. Sealed-tube samples for  $^1\text{H}$  NMR experiments were prepared on a high-vacuum line by condensing solvent and silane or HX reagent into a tube containing the Ir(I) complex.

$^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker MH-400 spectrometer at 400.13 and 162.00 MHz, respectively, and  $^{13}\text{C}$  NMR spectra were recorded on a Nicolet QE-300 spectrometer at 75.48 MHz. Chemical shifts were generally calculated from residual solvent resonances (acetone-d<sub>6</sub> 2.0 ppm, benzene-d<sub>6</sub> 7.15,  $\delta_{\text{C}}$  128.0). IR spectra were recorded on a Perkin-Elmer 467 spectrometer. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were recorded on a DuPont 21-490 B mass spectrometer.

Reaction of  $\text{IrBr}(\text{CO})(\text{dppe})$  with  $\text{Et}_3\text{SiH}$ . The reaction was carried out in a sealed NMR tube by first placing 7 mg of  $\text{IrBr}(\text{CO})(\text{dppe})$  in a 5-mm tube attached to a 1/4"20 glass joint. On a high-vacuum line 0.5 mL of solvent (benzene or acetone) and the desired amount of  $\text{Et}_3\text{SiH}$  were condensed into the tube at  $-196^\circ\text{C}$ , and the tube flame sealed. After thawing, the progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. The isomerized product,  $\text{IrHBr}(\text{SiEt}_3)^{-}$

in  $\text{C}_6\text{D}_6$  solvent, was isolated as a white powder from benzene-pentane solution. Found: C, 43.7%; H, 4.8%; P, 7.80.

#### Reaction of $\text{IrBr}(\text{CO})(\text{dppe})$ with $\text{Ph}_3\text{SiH}$ , $(\text{EtO})_3\text{SiH}$ , $\text{Me}_2\text{C}_2\text{SiH}$ , and $\text{MeC}_2\text{SiH}$

$^1\text{H}$  NMR studies of these reactions were carried out in nitrogen-purged  $\text{C}_6\text{D}_6$  solvent using typically 3 mg of  $\text{IrBr}(\text{CO})(\text{dppe})$  and 1-2 equivalents of 31.1 ml. in  $\text{C}_6\text{D}_6$  solvent.

**Reaction of  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$  with  $\text{Et}_3\text{SiH}$ .** The complex  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$  was prepared *in situ* by combining 0.5 ml. of acetone into an NMR tube containing 1.1 mmol. of  $\text{IrBr}(\text{CO})(\text{dppe})$  and 6.7 ml. (0.12 mmol.) of  $\text{PPN}(\text{CN})$ .<sup>1</sup> The mixture was shaken for one minute at room temperature to give a homogeneous solution. After cooling to -196°C.,  $\text{Et}_3\text{SiH}$  was condensed in with the tube, flamed, and the tube was sealed.

**Reaction of  $\text{IrBr}(\text{CO})(\text{dppe})$  with  $\text{HI}$ .** A  $\text{C}_6\text{D}_6$  solution of  $\text{IrBr}(\text{CO})(\text{dppe})$  in 1.5 mm NMR tube was purged with the gas evolved from the reaction of NaI with concentrated sulfuric acid using a nitrogen flow. This procedure, while not efficient for generating  $\text{H}(\text{g})$ , proved adequate for this experiment.

#### Reaction of $\text{Ir}(\text{CO})(\text{dppe})$ with $\text{HBr}$ .

0.1 ml. (5 equiv) of HBr (99.8%) was added via syringe to a  $\text{C}_6\text{D}_6$  solution containing 1 mg of  $\text{Ir}(\text{CO})(\text{dppe})$  in a septum-capped NMR tube and the sample was analyzed by  $^1\text{H}$  NMR spectroscopy.

**Preparation of  $\text{IrHBr}_2(\text{CO})(\text{dppe})$ .** 1 ml. (0.011 mmol) of 47% HBr was added to 1.0 ml. of an orange benzene solution containing 0.1 mg (0.071 mmol) of  $\text{IrBr}(\text{CO})(\text{dppe})$ . The mixture was stirred for 2 hours during which a light yellow precipitate formed and the solution turned nearly colorless. The precipitate was collected by filtration and washed with benzene to give 41 mg (7.1%) of  $\text{IrHBr}_2(\text{CO})(\text{dppe})$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$ -ether gave a cream-colored precipitate. Anal. Calcd. for  $\text{IrHBr}_2(\text{CO})(\text{dppe})$ : C, 41.60; H, 3.23; P, 7.93. Found: C, 41.60; H, 3.53; P, 7.93.

#### Results and Discussion

All of the oxidative addition reactions and subsequent chemistry described here were followed by  $^1\text{H}$  NMR spectroscopy. The chemical shifts and splitting patterns of the hydride resonances provide in almost all cases unambiguous assignment of the stereochemistry of the oxidative addition products.

As noted above, concerted *cis* addition of HY to the  $\text{Ir}(\text{I})$  complexes  $\text{IrX}(\text{CO})(\text{dppe})$  yields in principle four different stereoisomers. These arise from oxidative addition of HY to the square plane by either pathway I or II, each with either of two possible substrate orientations for the concerted process. For stereoisomers I- $\text{HC}$  and II- $\text{HX}$ , the hydride resonance shows *cis* coupling to two nonequivalent phosphines, and a chemical shift distinctive for the ligand *trans* to hydride. For stereoisomers I- $\text{HP}$  and II- $\text{HP}$ , the hydride resonance occurs in the range -7.7 to -8.6 ppm with a distinctive doublet of doublets pattern and large *trans* J<sub>PH</sub>. The magnitude of this *trans* coupling, together with previously established reaction chemistry, provides the basis for distinguishing between stereoisomers I- $\text{HP}$  and II- $\text{HP}$ .

**Reaction of  $\text{Et}_3\text{SiH}$  with  $\text{IrBr}(\text{CO})(\text{dppe})$ .** A benzene sample of  $\text{IrBr}(\text{CO})(\text{dppe})$  and three equivalents of  $\text{Et}_3\text{SiH}$  yields a pale yellow solution after thawing and shaking for one minute, indicating nearly complete reaction of the orange-colored  $\text{Ir}(\text{I})$  compound  $\text{IrBr}(\text{CO})(\text{dppe})$ . The  $^1\text{H}$  NMR spectrum taken three minutes after thawing shows resonances assignable to two complexes of the type  $\text{IrHBr}(\text{SiEt}_3)(\text{CO})(\text{dppe})$  along with peaks for unreacted  $\text{Et}_3\text{SiH}$  (NMR and IR data are collected in Table I). The hydride resonances appear as an approximate triplet at  $\delta$  -8.48 containing two nearly equivalent *cis* phosphorus couplings (-17.8 Hz), and a doublet of doublets at  $\delta$  -16.64 containing two *cis* phosphorus couplings (5.8 and 15.1 Hz).

The relative amounts of the two hydride products are 30% ( $\delta$  -8.48) and 62% ( $\delta$  -16.64). Over the course of 20 minutes the hydride product crystallized and was collected by filtration and washed with benzene to give 41 mg (7.1%) of  $\text{IrHBr}_2(\text{CO})(\text{dppe})$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$ -ether gave a cream-colored precipitate. Anal. Calcd. for  $\text{IrHBr}_2(\text{CO})(\text{dppe})$ : C, 41.60; H, 3.23; P, 7.93. Found: C, 41.60; H, 3.53; P, 7.93.

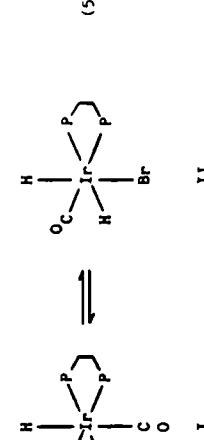
resonance at  $\delta$  -8.48 disappears as the  $\delta$  -16.64 peak becomes larger and a new hydride resonance at  $\delta$  -8.34 (dd,  $J_{PH}$  = 8.5, 153.5 Hz) appears. After 10 minutes an apparent equilibrium has been reached between the  $\delta$  -16.64 complex (1a) and the  $\delta$  -8.34 species (2a). Figure 1 shows  $^1H$  NMR spectra of the reaction of  $IrBr(CO)(dppc)$  with 1.25 equivalents of  $Et_3SiH$ . The first spectrum was taken after three minutes of reaction at 8°C and consists mainly of resonances assigned to the kinetic product with the hydride multiplet at  $\delta$  -8.48 (see Table I for peak assignments). The second spectrum was taken after several hours of reaction at 25°C and contains predominantly the thermodynamic product with the hydride resonance at  $\delta$  -16.64.

Similar results are obtained when the reaction is carried out in acetone solution. After three minutes two hydride resonances are observed at  $\delta$  -8.73 (t,  $J_{PH}$  = 17.9 Hz) and  $\delta$  -10.96 (dd,  $J_{PH}$  = 5.9, 15.3 Hz) in the relative amounts 76% and 24%, respectively, while a third hydride species appears over the course of an hour at  $\delta$  -8.86 (dd,  $J_{PH}$  = 8.5, 151 Hz) as the mixture reaches an equilibrium. After 54 hours, the composition of hydride species in the acetone solution corresponds to 3.5% of the  $\delta$  -8.73 compound, 88% of the  $\delta$  -16.96 compound, and 8.5% of the  $\delta$  -8.86 species. The three hydride resonances at  $\delta$  -8.73, -16.96, and -8.86 in acetone and at  $\delta$  -8.48, -16.64, and -8.34 in benzene are assigned to 1a, 2a, and 3a, respectively, in eqn (4).

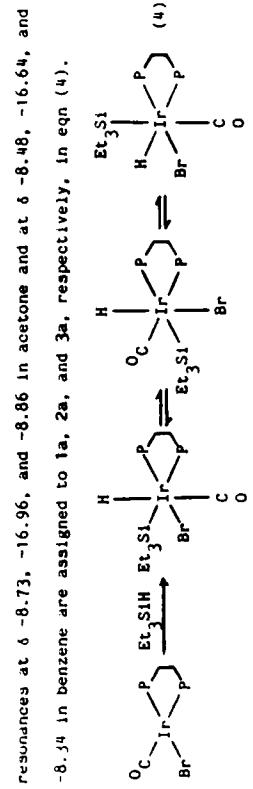
The stereoselectivity of  $Et_3SiH$  addition to  $IrBr(CO)(dppc)$  has also been examined at -33°C in acetone solution by  $^{31}P$  NMR spectroscopy. Initially, only

resonances assigned to 1a are observed at  $\delta$  35.9 and 16.8, indicating that the amount of 2a present must be  $\leq 1\%$ . Upon warming, new resonances appear at  $\delta$  27.3 and 24.3 for isomer 2a. Selective  $^1H$  decoupling experiments confirm that none of the observed resonances assigned to 1a and 2a are coupled to a tri- $n$ -butylphosphine ligand.

The rapid formation of 1a and slower formation of 2a parallels exactly the chemistry seen in the oxidative addition of  $H_2$  to  $IrX(CO)(dppc)$ , shown in eqn (5) for  $X = Cl$ , Br, and I. For both  $Et_3SiH$  and  $H_2$ , oxidative addition proceeds under kinetic control along the P-Ir-CO axis of  $IrX(CO)(dppc)$  (pathway 1 in eqns (1) and (3)), and then isomerization occurs forming the thermodynamically preferred isomer (2a or II) which corresponds to oxidative addition along the P-Ir-X axis (pathway II). An additional stereochemical feature of the  $Et_3SiH$  reaction is that although two substrate orientations are possible for each pathway of addition, the reaction kinetically favors the isomers that have mutually trans silyl and phosphine ligands, i.e., the NC product in pathway 1 (1a) and the HX product in pathway II (2a). The hydride resonances in 1a and 2a agree closely in chemical shift and  $J_{PH}$  coupling constants with the corresponding hydride resonances in I and II of eqn (5) (see Table I).

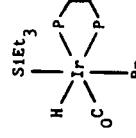


The assignment of structure 3a for the third product, which exhibits a hydride resonance at  $\delta$  -8.34 in benzene and -8.86 in acetone and remains a minor isomer, is based on the magnitude of  $J_{PH(trans)}$ . Examination of Table I shows



The stereoselectivity of  $Et_3SiH$  addition to  $IrBr(CO)(dppc)$  has also been examined at -33°C in acetone solution by  $^{31}P$  NMR spectroscopy. Initially, only

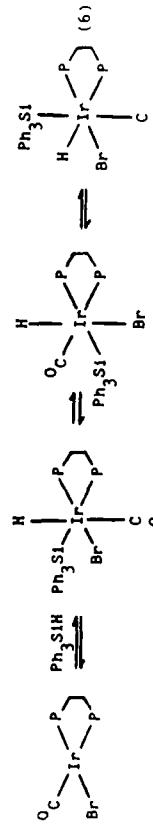
that the observed  $J_{PH}$  of 151 Hz (acetone) and 153.5 Hz (benzene) agrees more closely with *trans*  $J_{PH}$  of 152.2 Hz seen in **I** than with the corresponding value of 132.9 Hz in **II**. Structure **3a** arises from the oxidative addition of  $Et_3SiH$  along the kinetically preferred direction of addition, pathway **I**, but with the *HP* substrate orientation. The alternative assignment for this product is structure **4a** which would result from oxidative addition in the less favorable direction, pathway **II**, with the *HP* substrate orientation. We think this is a less likely possibility. While the assignment of **3a** to the third product

**4a**

formed in the reaction between  $Et_3SiH$  and  $IrBr(CO)(dppe)$  is not unambiguous, the assignment does not affect analysis of the kinetic diastereoselectivity of the reaction leading to **1a** over the thermodynamically most stable isomer **2a**.

#### Reaction of $Ph_3SiH$ , $(EtO)_3SiH$ , $Me_2ClSiH$ , and $MeCl_2SiH$ with $IrBr(CO)(dppe)$ .

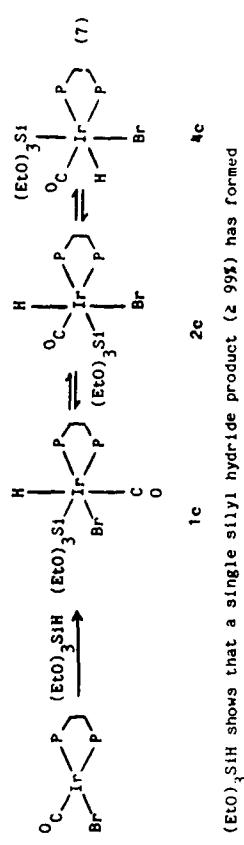
The reaction of  $IrBr(CO)(dppe)$  with  $Ph_3SiH$  also leads to the formation of three isomers of  $IrHBr(Ph_3Si)(CO)(dppe)$ , **1b**, **2b**, and **3b**, eqn (6). Six minutes after

**1b****2b****3b**

adding benzene to  $IrBr(CO)(dppe)$  and three equivalents of  $Ph_3SiH$  the  $^1H$  NMR spectrum shows two hydride resonances at  $\delta$  -7.98 (dd,  $J_{PH}$  = 16.7, 19.1 Hz) and  $\delta$  -15.97 (dd,  $J_{PH}$  = 6.5, 17.0 Hz) assigned to isomers **1b** and **2b**, respectively, by analogy to the corresponding triethylsilyl compounds **1a** and **2a** (see Table I).

The relative amounts of **1b** and **2b** are 91% and 9% in the spectrum at t=6 min. Isomerization to a mixture of three isomers occurs over several hours, eventually reaching an equilibrium of 2% **1b**, 93% **2b**, and 5% **3b**. Complex **3b** is characterized by a hydride resonance at  $\delta$  -7.91 (dd,  $J_{PH}$  = 8.0, 151.9 Hz). The isomerization reaction follows first-order kinetics for the disappearance of **1b** until approaching equilibrium with  $k$  = 0.015 min $^{-1}$  at 23°C.

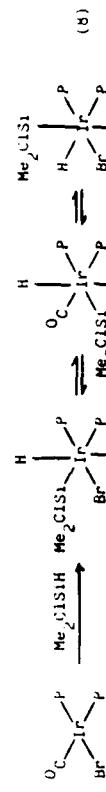
The reaction of  $IrBr(CO)(dppe)$  with  $(EtO)_3SiH$  follows a similar pattern where kinetic isomer **1c** forms initially and then isomerizes to an equilibrium mixture of three isomers, eqn (7). In this case, unequivocal assignments for the three isomers can be made based on a combination of  $^1H$  and  $^{13}C$  NMR experiments.  $^{13}CO$ -enriched  $IrBr(CO)(dppe)$  (88%  $^{13}CO$ ) was prepared by stirring a THF solution of  $IrBr(CO)(dppe)$  under  $^{13}CO$  at 50°C for 10 minutes and then precipitating the product. In the experiment using unlabeled  $IrBr(CO)(dppe)$ , the  $^1H$  NMR spectrum taken six minutes after the addition of one equivalent of



$(EtO)_3SiH$  shows that a single silyl hydride product (2 99%) has formed characterized by a hydride resonance at  $\delta$  -8.51 ( $\delta$ ,  $J_{PH}$  = 18.2 Hz). In the

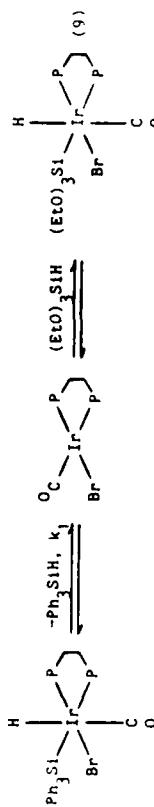
parallel experiment using  $^{13}\text{CO}$ -enriched  $\text{IrBr}(\text{CO})(\text{dppe})$ , the hydride resonance appears at  $\delta$  8.50 and contains an additional doublet splitting of 42.8 Hz due to coupling to the trans  $^{13}\text{CO}$  ligand as expected for isomer 1c. The  $^{13}\text{C}$  NMR spectrum shows a resonance at  $\delta$  176.8 (d of -t,  $J_{\text{HC}} = 42.8$  Hz,  $J_{\text{PC}} = 4.2$  Hz) and  $^1\text{H}$  decoupling confirms that the 42.8 Hz coupling is due to the hydride ligand. Complex 1c isomerizes much more slowly than the triethylsilyl and triphenylsilyl derivatives with a half-life of 45 hours at room temperature. The thermodynamic product 2c is characterized by a hydride resonance at  $\delta$  -16.49 (dd,  $J_{\text{PH}} = 6.7$ , 15.4 Hz). In the  $^{13}\text{CO}$ -enriched sample, this resonance contains an additional doublet splitting of 4.6 Hz due to the cis  $^{13}\text{CO}$  ligand. The  $^{13}\text{CO}$  resonance for 2c appears at  $\delta$  175.01 (dd,  $J_{\text{HC}} = 4.6$  Hz,  $J_{\text{PC}} = 6.7$ , 118.7 Hz). The large phosphorus-carbon coupling confirms that the ligands are trans to each other. The third isomer formed must be 4c based on the phosphorus coupling constants of the hydride resonance at  $\delta$  -8.32 (dd,  $J_{\text{PH}} = 17.4$ , 127.6 Hz) and the  $^{13}\text{C}$  NMR spectrum. The  $J_{\text{PH}}$  values compare favorably with those for the corresponding hydride in complex II ( $J_{\text{PH}} = 17.2$ , 132.9 Hz), and differ considerably from the couplings observed for diastereoisomers 3a ( $J_{\text{PH}} = 8.5$ , 153.5 Hz) and 3b ( $J_{\text{PH}} = 8.0$ , 151.9 Hz) from other silane additions. The  $^{13}\text{CO}$  resonance for 4c appears at  $\delta$  175.17 (ddd,  $J_{\text{HC}} = 4.6$  Hz,  $J_{\text{PC}} = 6.3$ , 120 Hz), and the 120 Hz phosphorus-carbon coupling confirms that the CO ligand is trans to phosphorus. At equilibrium the three diastereoisomers for  $(\text{EtO})_3\text{SiH}$  addition are present in the relative amounts 55 1c, 76s 2c, and 19s 4c.

The reaction of  $\text{IrBr}(\text{CO})(\text{dppe})$  with  $\text{Me}_2\text{ClSiH}$  forms initially the kinetic product 1d which isomerizes upon heating ( $t_{1/2} = 20$  min at 72°C) to two other isomers assigned as 2d and 3d, eqn (8). The assignments are based on the  $^1\text{H}$  NMR data in Table I and comparison with those for the analogous  $\text{Et}_3\text{Si}$ ,  $\text{Ph}_3\text{Si}$ , and  $(\text{EtO})_3\text{Si}$  derivatives.



1d  $\xrightarrow{24}$  3d  
The oxidative addition of  $\text{Me}_2\text{ClSiH}$  to  $\text{IrBr}(\text{CO})(\text{dppe})$  yields the usual kinetic product, 1d (see NMR data in Table I), but unlike the other silyl hydride products, no isomerization is observed, even upon heating the sample for one hour at 74°C. It appears that the isomerization rates for 1a-e are influenced by the electronegativity of the substituents on silicon such that the more electronegative substituents Cl and OEt slow the rate of isomerization.

All four of the observed diastereomers of  $\text{IrHBr}(\text{SiR}_3)(\text{CO})(\text{dppe})$ , 1-4, contain cis hydride and silyl ligands, and can in principle form by cis oxidative addition of  $\text{R}_3\text{SiH}$  to  $\text{IrBr}(\text{CO})(\text{dppe})$ . If the isomerization of the initially formed diastereomer, 1, proceeds via reductive elimination of  $\text{R}_3\text{SiH}$ , followed by oxidative addition with different stereochemistry, then the rate of  $\text{R}_3\text{SiH}$  reductive elimination from 1 must be fast compared to the rate of isomerization in order to account for the observed diastereoselectivity of  $\text{R}_3\text{SiH}$ . To test this hypothesis, we have attempted to measure the rate of reductive elimination of  $\text{Ph}_3\text{SiH}$  from 1b by adding  $(\text{EtO})_3\text{SiH}$  to a benzene solution of 1b. A  $^1\text{H}$  NMR spectrum taken four minutes after addition of 3.5 equivalents of  $(\text{EtO})_3\text{SiH}$  shows only resonances for 1c and the amount of 1b present must be < 25 at this time. Assuming that the reaction proceeds via initial  $\text{Ph}_3\text{SiH}$  reductive elimination as in eqn (9), this result indicates that the half-life of  $\text{Ph}_3\text{SiH}$  reductive elimination at 23°C is



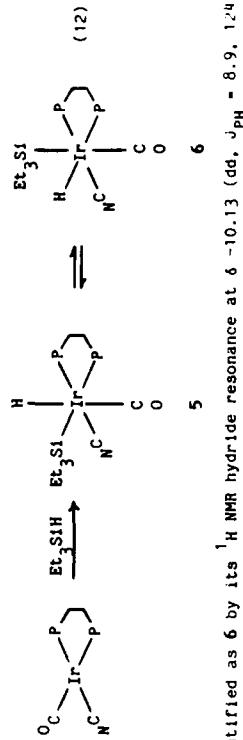
**1b** is much faster than the rate of isomerization,  $k_{\text{obs}}$ , the rate-determining step for eqn (10) must involve  $k_2$ . By applying the steady-state approximation to the intermediate  $[\text{IrBr}(\text{CO})(\text{dppe})]$  and ignoring  $k_2$ , we obtain the rate expression shown in eqn (11).

$$\text{rate} = k_{\text{obs}} [1b] = \frac{k_1 k_2}{k_{-1} + k_2} [1b] = \frac{k_1}{k_{-1}/k_2 + 1} [1b] \quad (11)$$

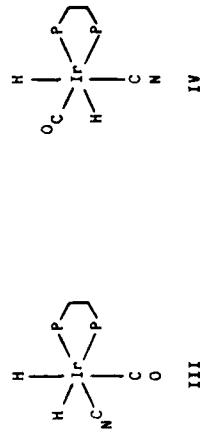
The diastereoselectivity of  $\text{Ph}_3\text{SiH}$  oxidative addition is  $k_{-1}/k_2$  and the observed result that  $k_1/k_{\text{obs}} \geq 50$  leads to the requirement that  $k_{-1}/k_2 \geq 50$ . This means that the minimum diastereoselectivity for the formation of **1a** over **2a** is 98%. Thus, while other first-order isomerization mechanisms cannot be ruled out, the two-step reductive elimination/oxidative addition mechanism in eqn (7) does

account for all of the experimental results, and appears most likely since the rate of  $\text{Ph}_3\text{SiH}$  reductive elimination is much faster than the rate of isomerization.

**Reaction of  $\text{Et}_3\text{SiH}$  with  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$ . Secondary Reaction of Iridium Triethylsilyl Hydride Complexes.** The complex  $\text{Ir}(\text{CH})(\text{CO})(\text{dppe})$  was prepared *in situ* from  $\text{IrBr}(\text{CO})(\text{dppe})$  and  $\text{PPN}(\text{CN})$  in acetone solution as reported previously,<sup>1</sup> and reacted with two equivalents of  $\text{Et}_3\text{SiH}$  in a sealed NMR tube. The <sup>1</sup>H NMR spectrum taken five minutes after thawing showed resonances for a single triethylsilyl hydride product.<sup>20</sup> Based on the hydride resonance at  $\delta = 10.05$  (*t*,  $\text{J}_{\text{PH}} = 17.3$  Hz) and other spectroscopic data in Table 1, the product is characterized as stereoisomer **5** in eqn (12). Over the course of several hours at room temperature **5** partially isomerizes to one other diastereomer



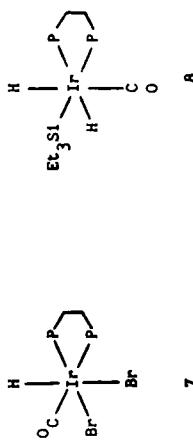
identified as **6** by its <sup>1</sup>H NMR hydride resonance at  $\delta = 10.13$  (dd,  $\text{J}_{\text{PH}} = 8.9, 1.24$  Hz). The two products, **5** and **6**, result from  $\text{Et}_3\text{SiH}$  oxidative addition to  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$  via pathway **1** with relative substrate orientations **HC** and **HP**, respectively. The stability of **5** and **6** relative to the diastereomers which would form via pathway **11** parallels closely the oxidative addition of  $\text{H}_2$  to  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$  where the kinetic isomer **III** is also the more stable isomer.<sup>1</sup> In this reaction, isomer **IV** which would result from  $\text{H}_2$  oxidative addition along the  $\text{P}-\text{Ir}-\text{CN}$  axis, pathway **11**, occurs as only a minor component at equilibrium. Thus, for the cyanide complex  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$  the same direction of oxidative



addition (pathway 1) is favored both kinetically and thermodynamically for the two substrates,  $\text{Fe}(\text{SiH}_3)_2$  and  $\text{H}_2$ .

In the later stages of the isomerization reaction of eqn (12), a secondary reaction is observed whereby the  $\text{IrH}_2(\text{CN})(\text{SiEt}_3)(\text{CO})(\text{dppb})$  stereoisomers 5 and 6 are converted to  $\text{IrH}_2(\text{CN})(\text{CO})(\text{dppb})$  (three isomers are in equilibrium<sup>14</sup>) with concomitant consumption of  $\text{Et}_3\text{SiH}$  and formation of  $\text{Et}_2\text{SiSiEt}_3$ . The  $^1\text{H}$  NMR spectrum after 3.5 hours shows new hydride peaks at  $\delta$  -10.11 and  $\delta$  -10.86 identical to those of compound III, and the relative amounts of products are 37, 5, 37, 6, and 26% III. After 25 hours there is 16% 5, 8% 6, and 76% isomers of  $\text{IrH}_2(\text{CN})(\text{CO})(\text{dppb})$ . Figure 2 shows  $^1\text{H}$  NMR spectra in the triethylsilyl region at different stages of the reaction. Eventually, ~95% of the triethylsilyl functional group is converted to  $\text{Et}_2\text{SiSiEt}_3$  ( $\delta$  0.94 (*t*,  $\text{CH}_3$ ,  $J$  = 7.9 Hz), 0.53 (*q*,  $\text{CH}_2$ ), two equivalents of  $\text{Et}_3\text{SiH}$  were used initially), at which time >90% of the triethylsilyl hydride species account for 100% ( $\text{CN}(\text{CO})(\text{dppb})$ ).

Examination of the  $\text{IrBr}(\text{CO})(\text{dppe}) + \text{Et}_3\text{SiH}$  samples, which were also prepared in sealed NMR tubes, reveals that secondary reaction chemistry is also occurring for the  $\text{IrBr}(\text{SiEt}_3)(\text{CO})(\text{dppe})$  isomers. The sample in acetone that originally contained  $\text{IrBr}(\text{CO})(\text{dppe})$  and one equivalent of  $\text{Et}_3\text{SiH}$  becomes orange-yellow in color while sitting in the dark at room temperature for one year, and the  $^1\text{H}$  NMR spectrum shows that the color is due to the regeneration of  $\text{IrBr}(\text{CO})(\text{dppe})$ . The complex  $\text{IrBr}(\text{CO})(\text{dppe})$  is identified by its four methylene resonances at  $\delta$  2.75, 2.68, 2.42, and 2.36 which integrate as 45% of the total dipe methylene peaks.

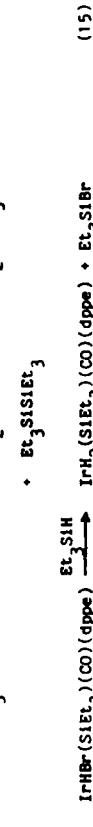
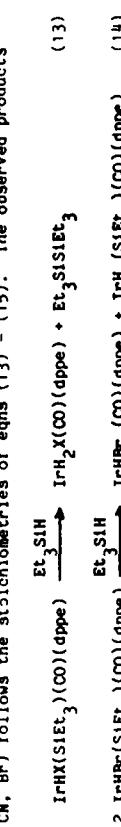


The triethylgermyl analog of **8**,  $\text{IrH}_2(\text{GeEt}_3)(\text{CO})(\text{dppe})$ , has been reported<sup>21</sup> and the  $^1\text{H}$  NMR spectra of the two compounds in benzene solution are very similar:  $\delta$ -10.04 (dd,  $J_{\text{PH}} = 11$ , 121 Hz), -10.82 ( $t$ ,  $J_{\text{PH}} = 19$  Hz) for the germyl compound, and  $\delta$ -10.02 (dd,  $J_{\text{PH}} = 11.0$ , 117.0 Hz), -10.69 ( $t$ ,  $J_{\text{PH}} = 19.1$  Hz) for the silyl compound. The initial organosilicon product is  $\text{Et}_3\text{SiSiEt}_3$  ( $\delta$  0.94 ( $t$ ,  $\text{CH}_3$ ,  $J = 8.0$  Hz), 0.53 ( $q$ ,  $\text{CH}_2$ )) while at longer times peaks apparently due to  $\text{Et}_3\text{SiOSiEt}_3$  appear ( $\delta$  0.94 ( $t$ ,  $\text{CH}_3$ ,  $J = 8.0$  Hz), 0.57 ( $q$ ,  $\text{CH}_2$ )).

Similar results are obtained for the sample in benzene prepared from  $\text{Ir}(\text{Br})(\text{CO})(\text{dppe})$  and three equivalents of  $\text{Et}_3\text{SiH}$ . After 25 days at room temperature the sample contains 75%  $\text{IrHBr}(\text{SiEt}_3)(\text{CO})(\text{dppe})$  (70.5% 2a and 4.5% 3a), 1%  $\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$  (II), 11%  $\text{IrHBr}_2(\text{CO})(\text{dppe})$  (7), and 13%  $\text{IrH}_2(\text{SiEt}_3)(\text{CO})(\text{dppe})$  (8). Upon further standing a small amount of colorless crystals forms as the hydride resonance for 7 diminishes. The amount of complex 8 continues to increase at the expense of 2a and 3a, and a new organosilicon product is observed,  $\text{Et}_3\text{SiBr}$  ( $\delta$  0.89 ( $\text{t}$ ,  $\text{CH}_3$ ,  $J = 7.8$  Hz), 0.67 ( $\text{q}$ ,  $\text{CH}_2$ ); mass spectrum, parent ions observed at  $m/z$  194, 196). After one year at room temperature a small amount of precipitate remains and the relative solution concentration of  $\text{Et}_3\text{SiBr}$  is 20% based on incorporation of hydride.

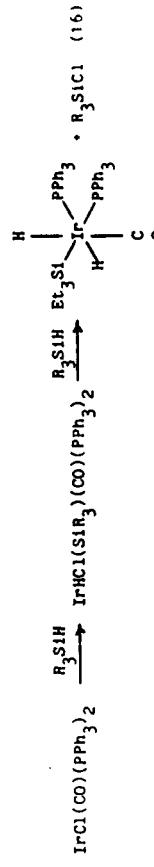
resonances is 16% II, 6% III, and 78% **8**. From analysis of the triethylsilyl spectral region (based on three equivalents of  $\text{Et}_3\text{SiH}$ ) there exists 0.54 equivalent of  $\text{Et}_3\text{SiBr}$ , 0.19 equivalent of  $\text{Et}_3\text{SiEt}_3$ , and 1.23 equivalents unreacted  $\text{Et}_3\text{SiH}$  (along with 0.72 equivalent of **8** and 0.15 equivalent of **2a**).

The secondary chemistry of the reaction systems  $\text{Ir}(\text{X}(\text{CO}))(\text{dppe}) + \text{Et}_3\text{SiH}$  (X =



can be accounted for within the framework of Ir(III)/Ir(I) reductive elimination/oxidative addition steps by the reactions in Scheme 1. Reductive elimination of HX from  $\text{IrH}(\text{SiEt}_3)(\text{CO})(\text{dppe})$  and subsequent reactions involving  $\text{Et}_3\text{SiH}$  and HX lead to either the formation of one equivalent each of  $\text{IrH}_2^X(\text{CO})(\text{dppe})$  and  $\text{Et}_3\text{SiSiEt}_3$  as in eqn (13), or the formation of equimolar amounts of  $\text{7}$ ,  $\text{8}$ , and  $\text{Et}_2\text{SiSiEt}_3$  as in eqn

(14). Eqn (15) represents an alternative route to **8** that does not result in  $\text{Et}_3^{\text{Si}}\text{Et}_3^{\text{S}}$  formation. In eqn (15) the reductive elimination of  $\text{Et}_3^{\text{Si}}\text{Br}$  from  $\text{IrHBr}(\text{SiEt}_3^{\text{S}})(\text{CO})(\text{dppe})$  is followed by  $\text{Et}_3^{\text{SiH}}$  oxidative addition to  $\text{IrH}(\text{CO})(\text{appe})$  yielding the silyl dihydride product. There is ample literature precedent for eqn (15) as both Clockling, et al.,<sup>10</sup> and Chalk<sup>6b</sup> have reported analogous chemistry with Vaska's complex, eqn. (16). The initial oxidative addition product,  $\text{IrHCl}(\text{SiEt}_3^{\text{S}})(\text{CO})(\text{PPh}_3)_2$ , has been isolated for  $\text{R} = \text{OEt}$  and **Cl**, **6a**,<sup>8</sup> and is



presumed to form for  $R = \text{Me}$  and  $\text{Et}$  as an unstable intermediate in eqn (16). Parish and coworkers<sup>8c</sup> have also proposed that  $\text{R}_3\text{SiCl}$  reductive elimination occurs from  $\text{IrHCl}(\text{SiR}_3)(\text{CO})(\text{PPh}_3)_2$  in catalytic H/D exchange reactions of  $\text{R}_3\text{SiH/D}_2$  and  $\text{R}_3\text{SiH/R}_3\text{SiD}$ . Vaska's complex reacts with trialkylgermanes in the same manner as eqn (16), giving  $\text{IrH}_2(\text{GeR}_3)(\text{CO})(\text{PPh}_3)_2$  and  $\text{R}_3\text{GeCl}$ , and, at longer times,  $\text{H}_2$  and  $\text{R}_3\text{GeCl}$ .<sup>21</sup> When the triethylphosphine derivative of Vaska's complex is used, the reaction is selective for digermane formation, eqn (17).



$\text{Et}_3\text{SiEt}_3$  is most likely formed via the intermediate  $\text{Ir}(\text{SiEt}_3)(\text{CO})(\text{dppe})$  which formally results from HX reductive elimination. It is not clear at this time whether unimolecular HX elimination occurs from  $\text{IrH}(\text{SiEt}_3)(\text{CO})(\text{dppe})$ , but, in a possibly related reaction, we have observed that the corresponding diaryliide complex II undergoes base-promoted dehydrohalogenation forming the intermediate

$\text{IrH}(\text{CO})(\text{dppe})$ .<sup>1</sup> Also noteworthy with regard to the intermediacy of  $\text{Ir}(\text{SEt}_3)(\text{CO})(\text{dppe})$  and  $\text{IrH}(\text{SEt}_3)_2(\text{CO})(\text{dppe})$  in Scheme I is the isolation of the *tert*-butyl  $\text{Ir}(1)$  compounds  $\text{Ir}(\text{GeEt}_3)(\text{CO})(\text{PPh}_3)_2$  ( $\text{R} = \text{Me, Et}$ ),<sup>21</sup> and the chelated diisyl hydride compound  $\text{IrH}(\text{SiMe}_2\text{OSiMe}_2)(\text{CO})(\text{PPh}_3)_2$  (prepared from Vaska's complex and  $\text{HMe}_2\text{SiOSiMe}_2\text{H}$ ).<sup>12</sup> Thus, reasonable precedents exist for all of the intermediates proposed in Scheme I.

**Reaction of  $\text{IrX}(\text{CO})(\text{dppe})$  with  $\text{HY}$  ( $\text{X} = \text{Br, I; Y = Br, I}$ ).** To an orange solution of  $\text{IrI}(\text{CO})(\text{dppe})$  in  $\text{C}_6\text{D}_6$  was added 5 equivalents of gaseous  $\text{HBr}$  giving a colorless solution which was analyzed by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum shows complete conversion to one major monohydride product which slowly interconverts with three other monohydride species (see Figure 3). Two of the later products are identified as  $\text{IrHBr}_2(\text{CO})(\text{dppe})$ , 7 ( $\delta = 15.38$  (dd,  $J_{\text{PH}} = 10.6$ , 15.6 Hz), and  $\text{IrH}_2(\text{CO})(\text{dppe})$ , 9 ( $\delta = 14.02$  (dd,  $J_{\text{PH}} = 8.7$ , 15.7 Hz), by independent syntheses from  $\text{IrX}(\text{CO})(\text{dppe})$  and  $\text{HX}$ . The other two products are characterized as isomers of  $\text{IrHBr}(\text{CO})(\text{dppe})$ , 10 and 11 in eqn (18), by the chemical shift and splitting pattern of the hydride resonances. Complex 10 has a hydride resonance at  $\delta = 13.39$  (dd,  $J_{\text{PH}} = 10.2$ , 15.9 Hz)

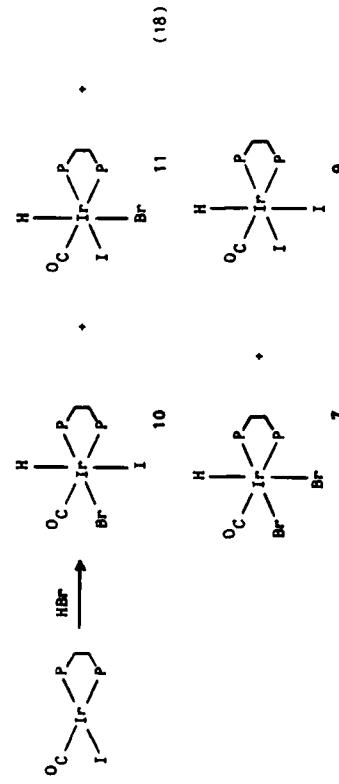
indicative of a hydride trans to iodide, while 11 has a hydride resonance at  $\delta = 15.99$  (dd,  $J_{\text{PH}} = 9.1$ , 15.5 Hz) indicative of a hydride trans to bromide. The similarity of the *cis* phosphorus-hydride coupling constants in the four hydride products is in accord with the common  $\text{IrH}_2(\text{CO})(\text{dppe})$  formulation where hydride is trans to  $\text{X}$ .

Complex 10 is the major initial product in reaction (18), comprising 86% of the mixture, and the other three products slowly increase in abundance over time as shown in Table II. After 500 hours the halide ligands in the four products are nearly randomly distributed (i.e., 25% of each product).

It is clear that of the two isomers of  $\text{IrHBrI}(\text{CO})(\text{dppe})$  observed in reaction (18), isomer 10 with *cis*  $\text{H}$  and  $\text{Br}$  ligands is formed preferentially relative to 11 which has *trans*  $\text{H}$  and  $\text{Br}$  ligands. Actually, there are six possible isomers for  $\text{IrHBrI}(\text{CO})(\text{dppe})$ , and based on the above experiment, one cannot rule out the possibility that 10 is a secondary product from the reaction of  $\text{IrI}(\text{CO})(\text{dppe})$  and  $\text{HBr}$ , and forms by isomerization of a different unobserved isomer.

To investigate this possibility we studied the reaction of  $\text{IrBr}(\text{CO})(\text{dppe})$  with  $\text{HI}$ . The same four products are observed, but now isomer 11 is the major product (70% of the product mixture according to the  $^1\text{H}$  NMR spectrum taken after 15 minutes, and only a small amount (~7%) of 10 is observed. The relative amounts of 7 and 9 are 10% and 13%, respectively. Thus the stereochemistry of the halides is reversed for the reaction of  $\text{IrBr}(\text{CO})(\text{dppe}) + \text{HI}$  compared to the reaction of  $\text{IrI}(\text{CO})(\text{dppe}) + \text{HBr}$ , a strong indication that the major product in each reaction is indeed the kinetic product.

The major product in each case of  $\text{HY}$  addition is the isomer that would be formed by a concerted *cis* addition of  $\text{HY}$  along the *P*- $\text{Ir}$ - $\text{X}$  axis in  $\text{IrX}(\text{CO})(\text{dppe})$ , corresponding to pathway 11 in eqn (3) with  $\text{HX}$  substrate orientation. This diastereoselection is opposite to that observed for both  $\text{R}_3\text{SiH}$  and  $\text{H}_2$ , which add along the *P*- $\text{Ir}$ -CO axis, pathway 1, and suggests that the initial interaction of



$\text{IrX}(\text{O})(\text{dppe})$  with  $\text{H}_2$  ( $\text{Y}$  = halide) differs significantly from that with  $\text{R}_3\text{SiH}$  or  $\text{H}_2$ .

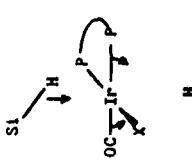
#### Mechanism of $\text{R}_3\text{SiH}$ and $\text{H}_2$ Oxidative Addition and Basis for Stereoselectivity.

The oxidative addition of  $\text{R}_3\text{SiH}$  to  $\text{IrX}(\text{CO})(\text{dppe})$  occurs by *cis* addition with kinetically controlled stereochemistry. The initially formed isomer in all cases corresponds to addition along pathway 1 with  $\text{HC}$  preferred substrate orientation. For  $\text{IrBr}(\text{CO})(\text{dppe})$ , rapid formation of the 1- $\text{HC}$  kinetic isomer is followed by slower formation of the isomer corresponding to pathway 11 addition with  $\text{HX}$  orientation. This latter isomer is the most stable of the four possible diastereomers of *cis* silane addition to  $\text{IrBr}(\text{CO})(\text{dppe})$ . In the case of  $\text{Ir}(\text{CH}_3)(\text{CO})(\text{dppe})$ , the same diastereoselectivity of silane addition is observed (>99.5% 1- $\text{HC}$  initially) but the relative stability of the diastereomers changes such that the kinetic isomer is also the most stable isomer.

With regard to both the kinetic diastereoselectivity and relative stability of product isomers, the oxidative addition of  $\text{R}_3\text{SiH}$  to  $\text{IrX}(\text{CO})(\text{dppe})$  shows remarkable parallels to that reported previously for  $\text{H}_2$ ,<sup>1</sup> strongly suggesting the same mechanism of addition for  $\text{R}_3\text{SiH}$  and  $\text{H}_2$ . In the prior analysis of  $\text{H}_2$  stereoselectivity, we discussed the preference for addition via pathway 1 over 11 in terms of  $\text{H}_2$  approach to the metal complex in a concerted process, and suggested two factors which would work to favor A ( $\text{H}_2$  parallel to  $\text{P}-\text{Ir}-\text{CO}$ ) over B ( $\text{H}_2$  parallel to  $\text{P}-\text{Ir}-\text{X}$ ). These factors are: (1) an orbital overlap effect wherein the  $\pi^*$  orbital of CO enhances the back-bonding interaction between a filled metal  $d_{\pi}$  orbital and  $\sigma^*(\text{H}_2)$  through increased overlap; and (2) a preferred bending of the set of trans ligands P and CO which become *cis* to each other and *trans* to the hydride ligands in the product. The latter factor is based on the notion that  $\text{H}_2$  addition to the metal complex is similar to forming an adduct with an electron pair donor. As the  $\text{H}_2$  substrate approaches the metal

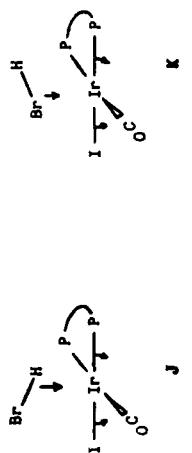
complex in this addition, one pair of trans ligands bends such that complex + substrate form a trigonal bipyramidal as the transition state. The bending ligands and the  $\text{H}_2$  substrate occupy the equatorial sites of this trigonal bipyramidal. Preference for bending of the  $\text{P}-\text{Ir}-\text{CO}$  axis over the  $\text{P}-\text{Ir}-\text{X}$  axis occurs because this places the better  $\pi$ -acid ligand CO in the equatorial plane where it can better stabilize the developing trigonal bipyramidal. This view is similar to that used to explain the *trans* effect in square planar substitution reactions,<sup>22</sup> and relates to the proposal put forth by Harrod<sup>3</sup> and shown as C that deformation of the square planar complex is a major component of the activation barrier in  $\text{H}_2$  oxidative addition. Both of the factors proposed to explain  $\text{H}_2$  stereoselectivity can be extended to silane oxidative addition as well.

The question of relative substrate orientation does not arise in the oxidative addition chemistry of  $\text{H}_2$  but must be addressed for silanes. For addition of  $\text{Si}-\text{H}$  along  $\text{P}-\text{Ir}-\text{CO}$ , pathway 1, the formation of the  $\text{HC}$  isomer as the kinetic isomer corresponds to a clear preference of  $\text{Si}-\text{H}$  approach shown in D to that shown in E. The basis of this preference is probably steric and involves minimizing non-bonded interactions between the silyl group and the phosphine substituents. Approach D makes the silyl group *cis* to only one of the phosphines and *trans* to the other. Similarly for addition along pathway 11, approach F is favored over G, leading to formation of the  $\text{HX}$  isomer with  $\text{R}_3\text{Si}$  *cis* to one P donor and *trans* to the other. Steric interactions may also alter silane approach to the metal complex such that the  $\text{Si}-\text{H}$  bond is not parallel to the  $\text{P}-\text{Ir}-\text{CO}$  axis but rather is tilted towards an "end-on" approach, H, which emphasizes the hydridic character and donor ability of the  $\text{Si}-\text{H}$  bond. Thus, the relative importance of bending the  $\text{P}-\text{Ir}-\text{CO}$  axis to stabilize the developing trigonal bipyramidal increases in H relative to D, while that of the overlap



effect involving  $\pi(\text{CO})$  and the back-bonding interaction between filled metal  $d$  and  $d^0(\text{Si}-\text{H})$  is significantly diminished. If the more end-on approach depicted in H does in fact occur for Si-H oxidative addition, then the observed stereochemical similarities of silane and  $\text{H}_2$  addition suggest that the second factor given above (i.e., the relative ease of bending trans ligands) is the more important factor in determining the observed diastereoselectivity for both substrates.

The observation that hydrogen halides oxidatively add to  $\text{IrX}(\text{CO})(\text{dppe})$  in the opposite direction, along the P-Ir-X axis, pathway II, clearly indicates that the ease of trans ligand deformation or bending in  $\text{IrX}(\text{CO})(\text{dppe})$  without regard to incoming substrate cannot by itself account for the stereoselectivity of these oxidative addition reactions. Thus, the complex-substrate interaction must be substantially different for HX vs.  $\text{H}_2$  and  $\text{R}_3\text{SiH}$ . The first question that must be addressed is whether the HX addition is concerted or proceeds in two or more discrete steps. The stereoselective nature of the reaction where H and X ligands occupy cis positions in the kinetic product strongly suggests a concerted mechanism. In such a mechanism, the approach of the highly polar species HX along the P-Ir-X axis of  $\text{Ir}(\text{CO})(\text{dppe})$  will undoubtedly be unsymmetrical, and can be either electrophilic or nucleophilic in character as shown in J and K, respectively. If HBr approach is nucleophilic as in K the



situation resembles that of silane approach H and similar considerations would apply regarding the diastereoselectivity. Thus, the developing trigonal bipyramidal or  $\text{Ir}(\text{CO})(\text{dppe}) + \text{HBr}$  would be more stable with the better  $\pi$ -acid CO in the equatorial plane than with iodide there, and the concerted addition of HBr would be expected to proceed along P-Ir-CO, pathway I. This expectation is contrary to what is observed.

For electrophilic approach J, the bending of P-Ir-I leads to a complex  $\pi$ -substrate trigonal bipyramidal having the better donor iodide in the equatorial plane thus enhancing the ability of Ir(I) to donate electrons to an incoming electrophile. It is well established that Ir(I) complexes can act as electron pair donors as in the reactions of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with  $\text{BF}_3$  and  $\text{NO}^+$ , and the oxidative addition reaction of  $\text{MeI}$ . In the present case, the donor ability of the Ir complex is better if P-Ir-X bends than if P-Ir-CO bends, and this leads to the observed diastereoselectivity. The primary interaction of hydrogen halides with  $\text{IrX}(\text{CO})(\text{dppe})$  in nonpolar media, while leading to concerted addition, clearly differs from that of  $\text{H}_2$  and  $\text{R}_3\text{SiH}$ . We conclude that in concerted oxidative addition reactions to cis phosphine analogs of Vaska's complex, the stereochemistry of addition (i.e., pathway I or II) can be controlled kinetically by the nucleophilic or electrophilic character of the substrate.

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#### References and Notes

1. Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* in the press.
2. Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* 1983, 105, 7172-4.
3. Harrod, J. F.; Smith, C. A.; Than, K. A. *J. Am. Chem. Soc.* 1972, 94, 8321-5.
4. (a) Fawcett, J. P.; Harrod, J. F. *J. Organomet. Chem.* 1976, 113, 245-8.  
(b) Fawcett, J. P.; Harrod, J. F. *Can. J. Chem.* 1976, 54, 3102-9. (c) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Ibid.* 1969, 47, 2205-8.
5. Harrod, J. F.; Smith, C. A. *J. Am. Chem. Soc.* 1970, 92, 2699-2701.
6. (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* 1965, 87, 16-21. (b) Chalk, A. J. *J. Chem. Soc., Chem. Commun.* 1969, 1207-8.
7. Bennett, M. A.; Charles, R.; Fraser, P. J. *Aust. J. Chem.* 1977, 30, 1201-11.
8. (a) Blackburn, S. N.; Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Chem. Research(S)* 1960, 170-1; *J. Chem. Research(H)* 1960, 2442-75. (b) Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Organomet. Chem.* 1973, 57, 279-85. (c) Blackburn, S. N.; Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Organomet. Chem.* 1980, 192, 329-38.
9. (a) Ebsworth, E. A. V.; Fraser, T. E.; Henderson, S. G.; Leitch, D. M.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* 1981, 1010-8. (b) Ebsworth, E. A. V.; Fraser, T. E. *Ibid.* 1979, 1960-8. (c) Ebsworth, E. A. V.; Leitch, D. M. *Ibid.* 1973, 1287-92. (d) Ebsworth, E. A. V.; Ferrier, H. M.; Fraser, T. E. *Ibid.* 1981, 836-9.
10. Glickling, F.; Irwin, J. G. *Inorg. Chim. Acta* 1972, 6, 355-8.
11. Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* 1969, 91, 7051-61.

12. (a) Curtis, M. D.; Greene, J. J. Am. Chem. Soc. **1978**, 100, 6362-7. (b) Gustavson, M. A.; Epstein, P. A.; Curtis, M. D. Organometallics **1982**, 1, 884-5. (c) Curtis, M. D.; Epstein, P. S. Adv. Organomet. Chem. **1981**, 19, 213-55.

13. Auburn, M. J.; Stobart, S. H. J. Chem. Soc., Chem. Commun. **1984**, 281-2.

14. (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapters 4, 6. (b) Harrod, J. F.; Chalk, A. J. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, pp 673-704. (c) Ojiam, I.; Yamamoto, K.; Kumada, M. In "Aspects of Homogeneous Catalysis"; Ugo, R., Ed.; D. Reidel: Boston, 1977; Vol. 3, pp 185-228.

15. Vaska, L. J. Am. Chem. Soc. **1966**, 88, 5323-7.

16. Blake, D. M.; Kubota, M. Inorg. Chem. **1970**, 9, 989-91.

17. Longato, B.; Morandini, F.; Bresadola, S. Inorg. Chim. Acta **1980**, 39, 27-34.

18. Martinsen, A.; Songstad, J. Acta Chem. Scand., Ser. A **1977**, A31, 645-50.

19. Fisher, B. J.; Eisenberg, R. Organometallics **1982**, 2, 764-7.

20. A small amount (4%) of a second hydride product characterized as  $\text{IrH}(\text{CN})_2(\text{SiEt}_3)(\text{dppe})^-$  with H trans to CN ( $\delta = 13.74$  (dd,  $J_{\text{PH}} = 12.3$ ,  $16.5$  Hz)) was also observed. This complex was independently prepared from  $\text{Ir}(\text{CN})_2(\text{CO})(\text{dppe})^-$  and  $\text{Et}_3\text{SiH}$ , indicating that its formation above was due to the use of a slight excess of  $\text{P}(\text{Ph})\text{CN}$  relative to  $\text{IrBr}(\text{CO})(\text{dppe})^-$ .

21. Clocking, F.; Wilbey, M. D. J. Chem. Soc. (A) **1970**, 1675-81.

22. (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th Ed.; Wiley: New York, 1980; p. 1201. (b) Huheey, J. E. "Inorganic Chemistry", 2nd Ed.; Harper and Row: New York, 1978; p. 496.

Scheme I

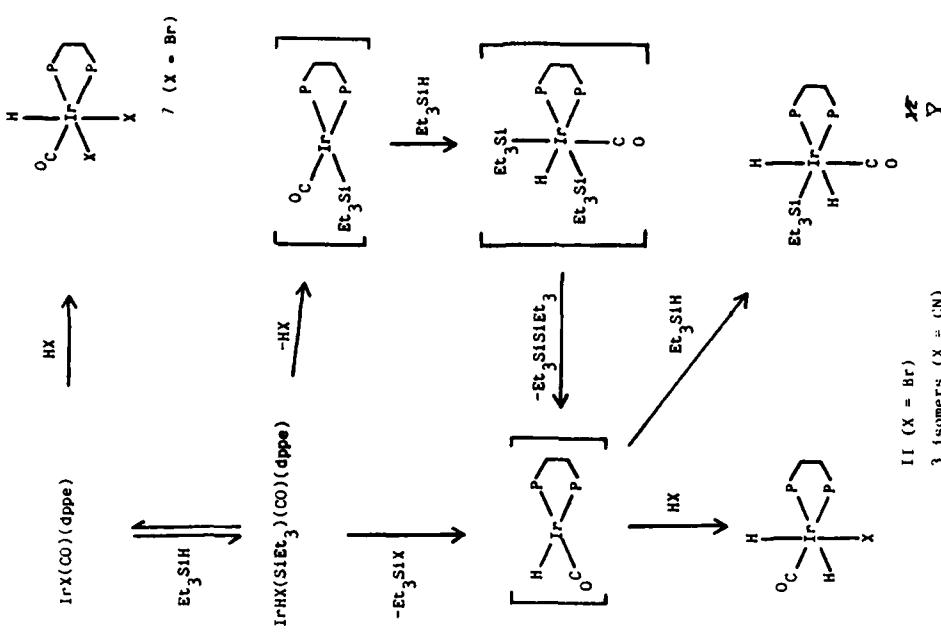


Table I.  $^1\text{H}$  NMR Data of Hydride Complexes.<sup>a</sup>

Compound	$\delta_{\text{IrH}}(\text{J}_{\text{PH}})$	$\delta_{\text{CH}_2}(\text{dppe})$	$\delta_{\text{O-Ph}}(\text{dppe})$	$\delta_{\text{R}}(\text{J}_{\text{PH}})$	IR $\text{HBr}(\text{SiEt}_3)(\text{CO})(\text{dppe})$ , 1a	IR $\text{HBr}(\text{SiMeC}_2)(\text{CO})(\text{dppe})$ , 1b	IR $\text{HBr}(\text{SiPh}_3)(\text{CO})(\text{dppe})$ , 1c	IR $\text{HBr}(\text{Si(OEt)}_3)(\text{CO})(\text{dppe})$ , 1d	IR $\text{HBr}(\text{SiPh}_2)(\text{CO})(\text{dppe})$ , 1e
Ir $\text{HBr}(\text{SiEt}_3)(\text{CO})(\text{dppe})$ , 1a	-8.48(-17.8)	2.02(1H) 1.83(2H) 1.49(1H) 3.02(1H) 2.20(2H) -1.22(1H) -8.34(8.5, 153.5)	8.02(2H) 7.77(2H) 7.53(4H) 7.85(2H) 7.57(4H) 7.46(2H)	1.39(3H) [12.381] 1.15(3H) 1.21(15H) 1.22(1H)	2d 2d -16.03(7.3, 14.1)	2.99(1H) 2.30(1H) 2.20(1H) 1.12(1H)	2.23(1H) 1.76(3H) 7.62(2H)	7.96(2H) 7.70(4H) 7.62(2H)	1.53(3H) 1.43(3H)
2a	-16.64(5.8, 15.1)	8.04(2H) 1.83(1H) 1.65(2H)	8.04(2H) 7.73(2H) 7.32(2H)	7.94(6H, o-Ph)				7.80(4H) 7.51(2H) 7.31(2H)	1.25(3H) 0.54(3H)
2b	-15.97(6.5, 17.0)	2.77(1H) 2.17(1H) 1.77(1H) 1.60(1H)	7.54(2H) 7.47(2H) 7.26(2H)	7.96(6H, o-Ph)				2.99(1H) 2.30(1H) 2.20(1H) 1.12(1H)	2.23(1H) 1.67(2H)
3b	-7.91(8.0, 151.9)							7.91(2H) 7.60-7.70(6H)	1.84(3H)
2c	-16.49(6.7, 15.4)	2.15(1H) 1.68-1.88(3H)	8.02(2H) 7.86(2H) 7.77(2H) 7.64(2H)	4.31(3H) 4.17(3H) 1.25(9H)				2.14(1H) 1.86(1H) 1.67(2H)	2.14(1H) 1.67(2H)
4c	-8.32(17.4, 127.6)	2.77(1H) 2.37(1H) 2.00(1H) 1.50(1H)	8.01(2H) 7.77(2H) 7.56(2H) 7.40(2H)	4.07(3H) 3.99(3H) 1.20(9H)				7.83(2H) 7.73(2H) 7.60(2H) 7.53(2H)	7.83(2H) 7.73(2H) 7.60(2H) 7.53(2H)

Table I. (continued)

Table I, continued

$\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$ ,	<b>10</b>	-13.59(10.2,15.9)	2.81(1H) 2.39(1H) 1.91(1H)	7.93(1H) 7.85(2H) 7.24(2H)
				7.27(2H)
	<b>11</b>	-15.99(9.1,15.5)		
$\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$ ,	<b>1</b>	-7.87(14.2,152.2) -8.94(-19.3)	2.29(1H) 2.10(1H) 2.05(1H) 1.75(1H)	8.09(2H) 7.97(2H) 7.79(2H) 7.27(2H)
				1.27(2H)
	<b>II</b>	-8.34(17.2,132.9) -17.48(8.6,16.6)	2.60(2H) 1.92(2H)	7.82(2H) 7.66(2H)
				7.56(2H)
				7.47(2H)
$\text{IrH}_2(\text{CN})(\text{CO})(\text{dppe})$ ,	<b>III<sup>d</sup></b>	-10.13(13.2,129.9) -10.87(-17.9)	3.25(1H) 2.88(2H) 2.50(1H)	7.97(4H) 7.88(2H) 7.67(2H)
	<b>IV<sup>d</sup></b>	-10.43(16.1,121) -13.27(12.5,19.3)		

Table I, Footnotes

<sup>a</sup> Spectra are taken from benzene solutions at 400 MHz unless otherwise indicated.<sup>b</sup> Spectrum taken at 6°C.<sup>c</sup> Resonance located by homonuclear decoupling experiments.<sup>d</sup> Acetone solution.<sup>e</sup>  $\text{CDCl}_3$  solution.Table II. Percent Composition of the Products from the Reaction of  $\text{Ir}(\text{L})(\text{CO})(\text{dppe})$  and HBr.

	Time,	$\text{IrHBr}(\text{CO})(\text{dppe})$	$\text{IrHBr}(\text{CO})(\text{dppe})$	$\text{IrHBr}_2(\text{CO})(\text{dppe})$	$\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$
	<i>h</i>	10	11	7	9
		0.1	86	4	6
		14	73	11	11
		41	66	11	15
		190	44	17	22
		550	31	22	25

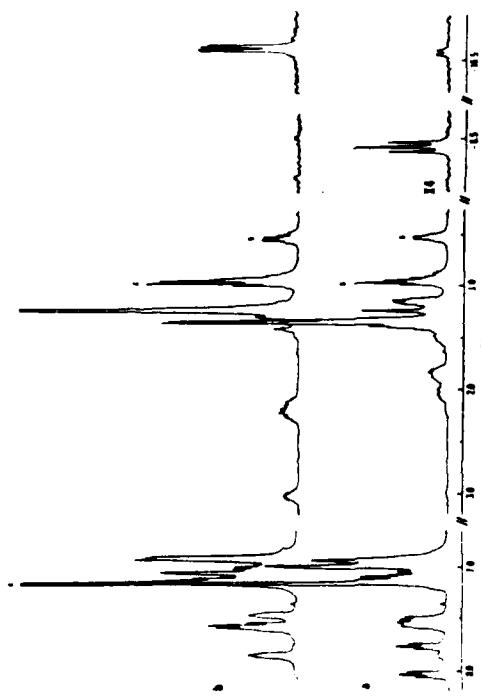


Figure 1.  $^1\text{H}$  NMR spectra of the reaction of  $\text{IrBr}(\text{CO})(\text{dppe})$  with  $\text{Et}_3\text{SiH}$  (a) after three minutes of reaction at  $8^\circ\text{C}$ ; (b) after several hours of reaction at  $25^\circ\text{C}$ . The peaks marked "S" are due to excess  $\text{Et}_3\text{SiH}$ , and the peak marked "x" corresponds to benzene solvent ( $\text{C}_6\text{D}_5\text{H}$ ,  $\delta$  7.15).

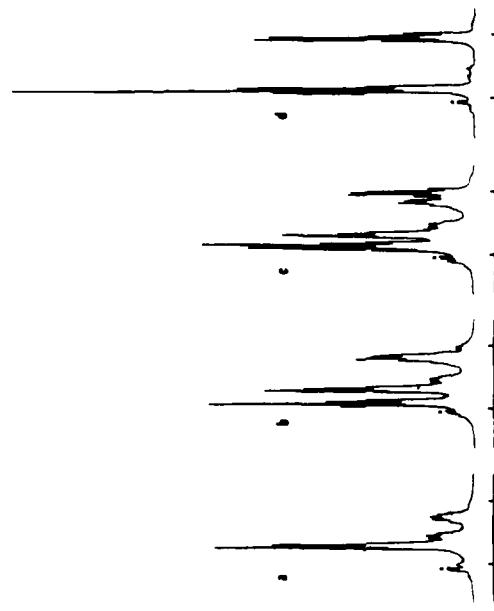


Figure 2.  $^1\text{H}$  NMR spectra in the triethylsilyl region for the reaction of  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$  and  $\text{Et}_3\text{SiH}$  in acetone solution: (a)  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe}) + 1.0$   $\text{Et}_3\text{SiH}$  after 5 minutes of reaction; (b)  $\text{Ir}(\text{CN})(\text{CO})(\text{dppe}) + 2.0$   $\text{Et}_3\text{SiH}$  after 12 minutes of reaction; (c) same sample at 207 minutes; (d) same sample after four months. The doublet marked "x" is due to a solvent impurity.

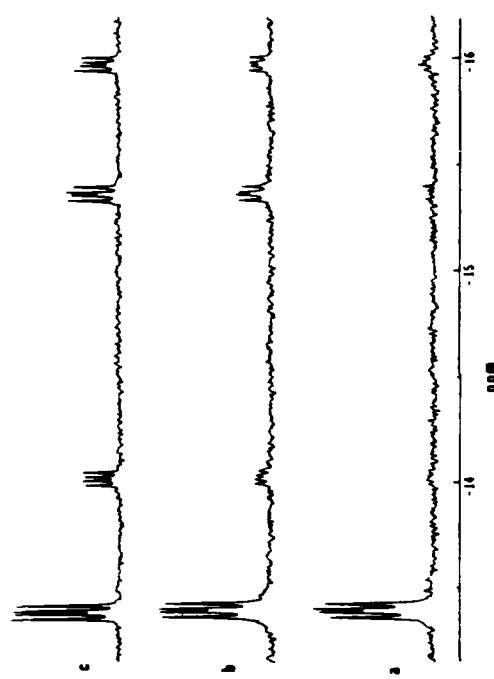


Figure 3.  $^1\text{H}$  NMR spectra in the hydride region for the reaction of  $\text{IrI}(\text{CO})(\text{dppe})$  with  $\text{HBr}(\text{g})$ : (a) after 38 minutes of reaction at 25°C; (b) 41 hours; (c) 190 hours.

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